AD676118

Technical Memorandum 1839

USE OF ORGANIC DYES IN WHITE SMOKE FORMULATIONS

by

Ralph Manno

September 1968

AMCMS Code 5542.15.54800
DA Project 1B542703D339-08

Pyrotechnics Laboratory
Feltman Research Laboratories
Picatinny Arsenal
Dover, New Jersey

TABLE OF CONTENTS

OBJECT

To investigate the use of dyes for the sustained production of white smoke clouds.

SUMMARY

Compositions containing potassium chlorate, sugar, vinyl alcohol acetate resin (VAAR), and the white dyes 2-chloroanthraquinone, and 1, 4, 5, 8-tetrachloroanthraquinone were found to produce good quality gray-white smoke clouds. With XM168 ground signal parts as test vehicles, the burning time of pressed pellets containing these dyes was between 16 and 25 seconds. Burning was slightly faster if granular rather than powdered dyes were used.

Compositions containing 2-chloroanthraquinone had an ignition temperature of 135°C, a temperature lower than desired for safe manufacture. An attempt to bring the ignition temperature up to a safer range by coating the ingredients with VAAR prior to the actual blending of the composition met with little success. Compositions containing 1, 4, 5, 8-tetrachloroanthraquinone had an acceptable ignition temperature of 305°C.

The impact sensitivity values were 8 inches for both compositions. Both were insensitive to friction.

A method for the selection of dye candidates suitable for smoke compositions was developed. With this technique, the quality of smoke display may be examined after heating the dye, or the smoke composition containing the dye.

CONCLUSIONS

1. Organic dye can be used to manufacture cool-burning smoke compositions which will produce gray-white clouds applicable for target marking or signaling.

2. A rapid method for selection of dye candidates suitable for smoke compositions has been developed.

3. Compositions containing 1, 4, 5, 8-tetrachloroanthraquinone are useful as white signals or markers. The same cannot be said of compositions containing 2-chloroanthraquinone. The greater thermal sensitivity of compositions containing 2-chloroanthraquinone may make manufacture of such compositions more hazardous, limiting their usefulness.

RECOMMENDATIONS

1. Compositions containing 1, 4, 5, 8-tetrachloroanthraquinone should be evaluated for use in the XM168 ground signal and in other applications where cool-burning white smoke compositions are desirable.

2. Further study and evaluation should be conducted on additional white dyes, including 1-chloroanthraquinone and 1, 5-dichloroanthraquinone.

INTRODUCTION

If an organic dye is mixed with an oxidizer such as potassium chlorate and a fuel such as sugar or sulfur, and the mixture is ignited, the heat produced by the reaction causes the dye to vaporize. Condensation of the dye in the atmosphere produces a colored cloud that may be used in signaling.

White smoke has been produced by the use of phosphorus and the so-called HC smokes. The former is extremely toxic and incendiary in nature. The HC smokes are based on the use of zinc or zinc oxide and a chlorinated organic compound. The earlier formulations, which used hexachloroethane, were found to be difficult to handle and unstable in the presence of moisture. Substitution of polyvinyl chloride and Dechlorane in the HC smokes improved the stability of the composition, but its other problems, such as excessive heat, destruction of metal parts, and unwanted incendiary action were still present.

Since a need for cool-burning white smokes exists, it was decided to investigate the feasibility of dye-based formulations. This report deals with such a study. The U. S. Naval Ammunition Depot, Crane, Indiana, has investigated the use of the dye 2-chloroanthraquinone to produce white smokes, but their investigation was very limited (Ref 1). However, the Naval Depot formulation appeared promising enough to select it for investigation together with several other dyes.

EXPERIMENTAL PROCEDURE

Smoke compositions were prepared by blending, using mortar and pestle, as described in Picatinny Arsenal SOP-PC 3, with alcohol as a dispersing medium. Cylindrical pellets, 0.85 inch in height, 1.125 inches in diameter, and weighing 18 grams each were formed from the composition, using a Stokes press. The pellets were assembled in the following manner: They were wrapped in 0.001-inch-thick aluminum foil and placed in a cylindrical aluminum container 1-5/8 inches high by 1-1/4 inches in diameter. Igniter cord was placed on the inside of the aluminum wrapping and in contact with the pellet. A cover cap was placed over the pellet and secured by a metal O-ring.

When testing the rounds, burning times were established with a stop watch, and smoke clouds were characterized using National Bureau of Standards color charts.

Ignition temperatures were obtained by differential thermal-analysis. Curves were obtained using a Fisher Differential Thermoanalyzer, Model 260 P. Chromel/alumel thermocouples were employed, and a heating rate of $10^{o}C$/minute was used.

RESULTS AND DISCUSSION

Compositions using dyes of the anthraquinone family have exhibited good quality clouds in many colored smoke formulations. Those using 2-chloroanthraquinone have been used by the U. S. Naval Ammunition Depot (Ref 1) in producing a white signal marker. However, no sensitivity data was available on these compositions. This dye and several other white dyes in the chloroanthraquinone group were screened and preselected for further study and evaluation. The screening procedure was conducted by wrapping 1 gram of dye or composition in aluminum foil and placing the sample in a cylindrical container. When the sample was heated on a hot plate, the dye vaporized and escaped through a 1/4-inch hole in the cover of the container. In the atmosphere the dye condensed and a colored cloud appeared.

This method may be modified by placing a beaker over the container, heating the sample for several minutes, and observing the smoke being formed. Condensed dye collected on the beaker wall or on an inserted microscope slide may subsequently be examined. In this laboratory technique, the use of a beaker to confine the smoke as it is generated results in high-temperature condensation of vaporized dye from the gas phase. Present nucleation theory indicates that the rate of dissipation of the latent heat of condensation-which is probably slow in the present technique, due to the elevated temperature of the confining atmosphere-affects the rate of nucleation and final particle size distribution. Consequently, the temperature of the confining atmosphere will be reduced in future studies so as to assure a more meaningful correlation with results expected in the field. Dyes evaluated by this technique were 1-choroanthraquinone, 2-chloroanthraquinone, 1, 5-dichloroanthraquinone, and 1, 4, 5, 8-tetrachloroanthraquinone. While all these dyes seemed to be good candidates for fur-

ther work, only 2-chloroanthraquinone and 1, 4, 5, 8-tetrachloroanthraquinone were investigated in this study. It is of interest to note that although a grayish-white smoke cloud is obtained using 1, 4, 5, 8-tetrachloroanthraquinone, the dye is pale yellow in appearance when incorporated into the composition, and after collecting on the beaker walls.

The experimental compositions used to produce a dye-based white smoke cloud are listed in Table 1, which also contains cloud characteristics such as volume, density, and color, as observed visually, and average burning time and rate for each composition. Details such as weight and size of pellets and a description of the vehicle used in testing are described under Experimental Procedure. The composition which produced most favorable results was SW 397, containing 55% 1, 4, 5, 8-tetrachloroanthraquinone, 27% potassium chlorate, 16% sugar, and 2% VAAR. The average burning time was 16 seconds; volume, density and color were good. Aluminum parts used in the test vehicles were unaffected by the burning of this composition.

The ignition temperature of SW 397 was determined to be 305°C. This temperature is considered satisfactory for the processing of the composition. The impact sensitivity of SW 397 (Table 2) was 8 inches using the Picatinny Arsenal Impact Apparatus (Ref 3); it was insensitive to friction when subjected to both steel and fiber shoe (Ref 4).

Compositions SW 391 and SW 393 were prepared using both fine and granular dyes (Table 2). These formulations contained 56% 2-chloroanthraquinone, 26% potassium chlorate, 16% sugar, and 2% VAAR. When granular dye was used (SW 393) the burning time of the composition was slightly faster than with the fine dye. The burning characteristics of both compositions remained the same with respect to color, volume, and density of smoke clouds. The advantages of using granular materials in handling and processing are well known, but manufacturing difficulties preclude the production of some dyes in that form.

The ignition temperatures of SW 391 and SW 393 were determined to be 135°C. Since 135°C is a relatively low value for smoke munitions, experiments were devised to attempt to raise the ignition temperature of the system to assure safe processing. In one experiment, 2-chloroanthraquinone was coated with VAAR and dried prior to

blending the composition; in another, the potassium chlorate was treated in the same manner. Both techniques raised the ignition temperature of the composition by 10°C, a value still considered lower than desired.

The low ignition temperatures of this composition may indicate that its manufacture is more hazardous than that of the colored smoke formulations currently used. It is considered that anything more hazardous to manufacture than the standard colored smoke compositions could not be advocated.

It was first thought that these low ignition temperatures were caused by a reaction between 2-chloroanthraquinone and potassium chlorate. However, when a differential thermal curve was run on the dye/oxidant binary, the ignition temperature was found to be 230°C. Subsequently, the ignition temperature of a 50/50 sugar/potassium chlorate binary was determined to be 142°C. Since the ignition temperatures of SW 391 and SW 393 were lower than those of either of the above binaries, it was concluded that an interaction among all the ingredients is responsible for the 135°C ignition temperature obtained.

LIST OF MATERIALS

1. 2-Chloroanthraquinone (MP, 210°C), North American Dye Corporation, Danbury, Connecticut; IFF-6-4712

2. 1,4,5,8-tetrachloroanthraquinone (MP, 340°C), General Dyestuff Co., Division of General Aniline and Film Corporation, New York

3. Potassium chlorate, Grade B, Class B, 20 ± 5 microns, Specification MIL-P-150, Hooker Chemical Co., New York

4. Sugar, Confectioners, XXXXXX, 10 ± 5 microns, Specification JJJ-S-7913, National Sugar Refining Co., New York

5. Vinyl Alcohol Acetate Resin (VAAR), MA-28-18, Union Carbide Plastics Co., New York

REFERENCES

1. Bliss, B. R., U. S. Naval Ammunition Depot, Crane, Indiana. RDTR 67, 5 August 1965

2. Clear, A. J., Standard Laboratory Procedures for Sensitivity, Brisance, and Stability of Explosives, Technical Report FRL-TR-25, Feltman Research Laboratories, Picatinny Arsenal, Dover, N. J., January 1961

3. Picatinny Arsenal Test Manual No. 7-1

TABLE 1

Burning characteristics of smoke compositions [a]

Composition Number	Ingredients		Average Burning Time, sec	Average Burning Rate in./min.	Volume	Density	NBS Color Chart
SW 391	2-Chloroanthraquinone (fine)	56	25	1.92	Good	Good	No. 263
	Potassium chlorate 20 ± 5 microns	26					
	Sugar, - Confectioners 6X	16					
	VAAR	2					
SW 393	2-Chloroanthraquinone (granular)	56	22	2.16	Good	Good	No. 263
	Potassium Chlorate 20 ± 5 microns	26					
	Sugar, - Confectioners 6X	16					
	VAAR	2					
SW 397	1,4,5,8-tetrachloroanthraquinone	55	16	3.0	Good	Good	No. 264
	Potassium chlorate 20 ± 5 microns	27					
	Sugar, - Confectioners 6X	16					
	VAAR	2					

[a] Data obtained using XM168 ground signal parts as test vehicles

TABLE 2

Sensitivity data for white smoke compositions

Formulation	Ignition Temp, °C[c]	Impact Sensitivity, inches (Ref 2)	Pendulum Test Friction Sensitivity: Steel Shoe	Pendulum Test Friction Sensitivity: Fiber Shoe (Ref 3)
SW 391	135	-	-	-
SW 393	135	8	NA	NA
SW 393[a]	145	-	-	-
SW 393[b]	145	-	-	-
SW 397	305	8	NA	NA
Sugar/$KClO_3$	142	-	-	-
2-Chloroanthraquinone/$KClO_3$	230	-	-	-

[a] VAAR-coated dye

[b] VAAR-coated $KClO_3$

[c] Ignition temperatures (DTA) reproducible to ± 5°C.

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Picatinny Arsenal, Dover, New Jersey	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

USE OF ORGANIC DYES IN WHITE SMOKE FORMULATIONS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

5. AUTHOR(S) (First name, middle initial, last name)

Ralph Manno

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
September 1968	14	4

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. DA Project 1B542703D339-08	Technical Memorandum 1839
c. AMCMS Code 5542.15.54800	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY

13. ABSTRACT

Compositions containing potassium chlorate, sugar, vinyl alcohol acetate resin (VAAR), and the white dyes 2-chloroanthraquinone, and 1, 4, 5, 8-tetrachloranthraquinone were found to produce good quality gray-white smoke clouds. With XM168 ground signal parts as test vehicles, the burning time of pressed pellets containing these dyes was between 16 and 25 seconds. Burning was slightly faster if granular rather than powdered dyes were used.

Compositions containing 2-chloroanthraquinone had an ignition temperature of 135°C, a temperature lower than desired for safe manufacture. An attempt to bring the ignition temperature up to a safer range by coating the ingredients with VAAR prior to the actual blending of the composition met with little success. Compositions containing 1, 4, 5, 8-tetrachloroanthraquinone had an acceptable ignition temperature of 305°C.

The impact sensitivity values were 8 inches for both compositions. Both were insensitive to friction.

DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED

Security Classification

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Pyrotechnics						
Organic dyes						
White smoke formulations						
XM168 ground signal						
2-Chloroanthraquinone						
1, 4, 5, 8-tetrachloroanthraquinone						
Vinyl alcohol acetate resin						
Potassium chlorate						
Impact sensitivity						
Friction sensitivity						

UNCLASSIFIED
Security Classification